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Passive Dosing of Pyrethroid Insecticides to *Daphnia magna*: Expressing Excess Toxicity by Chemical Activity

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Introduction and objectives

It is challenging to control and express exposure of hydrophobic organic compounds in aquatic toxicity experiments, due to the sorption of these compounds to vessel surfaces and organic material. In the current study, **passive dosing** was used to tightly control exposure throughout toxicity experiments [1], while **chemical activity** was used to express exposure and form basis for comparison of toxicity data [2].

This study addresses the acute toxicity of pyrethroid insecticides towards the aquatic invertebrate *Daphnia magna* and asks:

1. Is pyrethroid toxicity generally underestimated in the literature due to poorly controlled exposure?
2. At which chemical activity do pyrethroids exert their toxicity, and how similar are the median effect chemical activity (Ea_{50}) for different pyrethroids?
3. How much more toxic are pyrethroids relative to baseline toxicity?

Experimental

Passive dosing with silicone was used to set and maintain freely dissolved concentrations of α-cypermethrin, esfenvalerate and bifenthrin in 48-h immobilisation experiments with *Daphnia magna*.

- Silicone elastomer was cast in glass vials.
- Silicone was loaded with test compounds ($C_{silicone}$).
- Test organisms were exposed in water, continuously equilibrated with loaded silicone (C_{free}).
- $C_{free} = \frac{C_{silicone}}{K_{silicone:water}}$
- Experiments to determine partition ratios ($K_{silicone:water}$) for the specific silicone are ongoing.

Figure 1. Passive dosing experiments. 1: Pyrethroid loaded silicone and 2: Equilibrated water with *Daphnia magna*.

Results

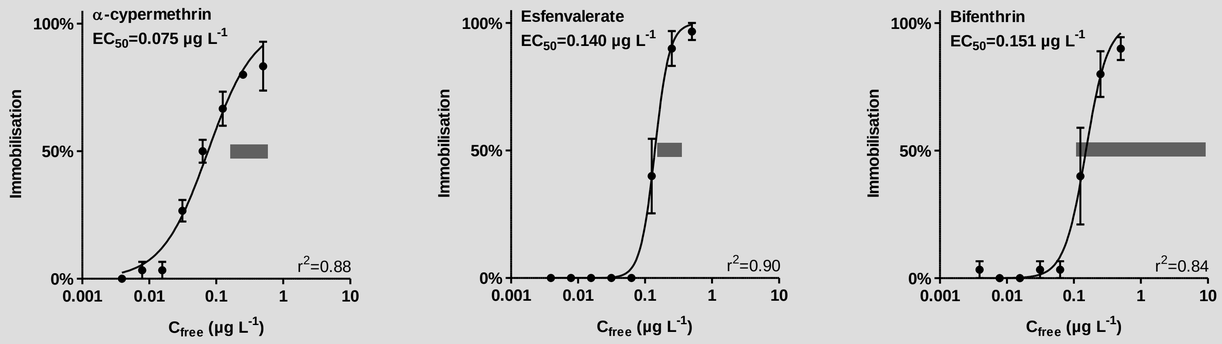

Figure 2. Immobilisation (%) of *Daphnia magna* after 48 h exposure to the three pyrethroids as a function of freely dissolved concentration (C_{free}, µg L^{-1}). The median effect concentrations (EC_{50}) are given, with ranges of literature EC_{50} values indicated by dark grey beams [3-12]. The EC_{50} values correspond to 180 pmol L^{-1} (95% CI: 149-219 pmol L^{-1}) for α-cypermethrin, 333 pmol L^{-1} (95% CI: 298-374 pmol L^{-1}) for esfenvalerate and 357 pmol L^{-1} (95% CI: 300-426 pmol L^{-1}) for bifenthrin. Error bars represent the standard error of the mean (n=6).

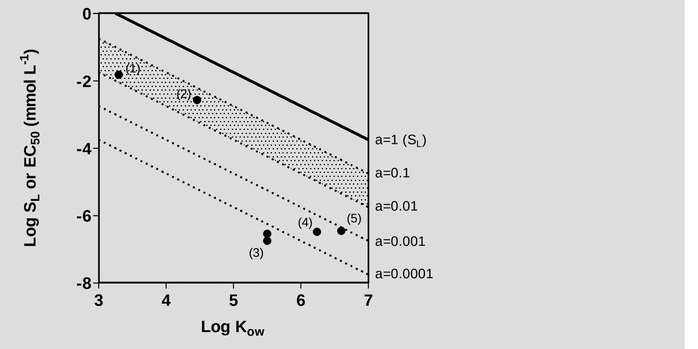

Figure 3. Regression of subcooled liquid solubility (S_L, mmol L^{-1}, solid line, [13]) and lines representing the chemical activity 0.1, 0.01, 0.001 and 0.0001 (a, unit less, broken lines). The shaded area is the chemical activity range 0.01 to 0.1 for the initiation of baseline toxicity. EC_{50} values of naphthalene (1)[1], phenanthrene (2)[1], α-cypermethrin (3), esfenvalerate (4) and bifenthrin (5) are plotted against their K_{OW} values. The median effect chemical activity (Ea_{50}) is ≈0.000032, ≈0.00032 and ≈0.00079 for α-cypermethrin, esfenvalerate and bifenthrin, respectively.

Conclusions

Based on current data, the following was concluded:

1. In general, the median effect concentrations (EC_{50}) were in agreement with lowest literature values (Figure 2), and these studies thereby validate each other. To the contrary, higher literature values seem to underestimate pyrethroid toxicity.
2. The three pyrethroids had median effect chemical activities (Ea_{50}) in the chemical activity range 0.00001 to 0.001 (Figure 3), corresponding to median immobilisation at 0.01 to 1‰ of the pyrethroid's subcooled liquid solubility. The Ea_{50} values were within 2 orders of magnitude.
3. The three pyrethroids were 1-3 orders of magnitude more toxic relative to baseline toxicity (Figure 3). In this way, excess toxicity was expressed by Ea_{50} values well below the chemical activity range 0.01 to 0.1 for the initiation of baseline toxicity.

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[1] Smith et al, 2010. Controlling and maintaining exposure of hydrophobic organic compounds in aquatic toxicity tests by passive dosing. *Aquat. Toxicol.* 98: 15-24. [2] Reichenberg and Mayer, 2006. Two complementary sides of bioavailability: Accessibility and chemical activity of organic contaminants in sediments and soils. *Environ. Toxicol. Chem.* 25: 1239-1245. [3] PPDB: Pesticide Properties DataBase, University of Hertfordshire, United Kingdom, http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm. [4] Pesticide Action Network (PAN) Pesticide Database, North America, http://www.pesticideinfo.org/. [5] ECOTOX Database, U.S. Environmental Protection Agency, U.S., http://cfpub.epa.gov/ecotox/. [6] Mokry and Hoagland, 1990. Acute toxicities of five synthetic pyrethroid insecticides to *Daphnia magna* and *Ceriodaphnia dubia*. *Environ. Toxicol. Chem.* 9: 1045-1051. [7] Ye et al, 2004. Effects of bifenthrin on *Daphnia magna* during chronic toxicity test and the recovery test. *J. Environ. Sci.* 16: 843-846. [8] Ma et al, 2009. Enantioselectivity in aquatic toxicity of synthetic pyrethroid insecticide fenvalerate. *Ecotox. Environ. Safe.* 72: 1913-1918. [9] Nørgaard and Cedergreen, 2010. Pesticide cocktails can interact synergistically on aquatic crustaceans. *Environ. Sci. Pollut. Res.* 17: 957-967. [10] Brausch et al, 2010. Effects of functionalized fullerenes on bifenthrin and tribufos toxicity to *Daphnia magna*: Survival, reproduction and growth rate. *Environ. Toxicol. Chem.* 29: 2600-2606. [11] Stampfli et al, 2011. Environmental context determines community sensitivity of freshwater zooplankton to a pesticide. *Aquat. Toxicol.* 104: 116-124. [12] Bjergager et al, 2012. Synergy between prochloraz and esfenvalerate in *Daphnia magna* from acute and subchronic exposures in the laboratory and microcosms. *Aquat. Toxicol.* 110: 17-24. [13] Mackay et al, 1980. Relationships between aqueous solubility and octanol-water partition coefficients. *Chemosphere* 9: 701-711.